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(54) **Polyoxymethylene multi-copolymer and its resin composition.**

(57) A polyoxymethylene multi-copolymer having spherulites and obtainable by copolymerizing

(a) trioxane,

(b) at least one cyclic ether or formal compound chosen from ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane and 1,3,6-trioxocane, and

(c) at least one compound chosen from glycidyl phenyl ether, styrene oxide and glycidyl naphthyl ether, is characterised in that the number average molecular weight of said polyoxymethylene multi-copolymer is from 10,000 to 100,000, that the melting point (T_m) and crystallization temperature (T_c) thereof are governed by the relationship,

$T_m - T_c < 15 (^{\circ}\text{C})$

and that the size of the spherulites is 10 μm or less, and a resin composition comprising such a polyoxymethylene multi-copolymer and a polyoxymethylene resin, are distinguished in their crystallinity, mechanical strength and surface appearance and are particularly suited for faster cycle molding.

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POLYOXYMETHYLENE MULTI-COPOLYMER AND ITS RESIN COMPOSITION.

Background of the Invention

This invention relates to a polyoxymethylene multi-copolymer distinguished in injection moldability, particularly its suitability for achieving a faster cycle performance and improved mechanical properties.

More specifically, this invention relates to a polyoxymethylene multi-copolymer used for injection molding which is distinguished in having a faster speed of solidification in the mold in injection molding to allow molding with the molding time reduced and also in its mechanical properties on account of the smaller size of spherulites present and consequently reduced molding strain.

The invention also relates to a polyoxymethylene resin composition distinguished in surface appearance, crystallinity, mechanical strength and molding efficiency.

Polyoxymethylene resins are known as engineering plastics well balanced in their mechanical strength and impact resistance and are used in a wide range of fields such as for automobile parts and electronic equipment parts.

However, polyoxymethylene resins in general have a very high crystallinity due to growth of the spherulite structure which as a result produces cracking or internal tension to reduce the mechanical strength of moldings produced from the resin.

Furthermore, the polyoxymethylene resins are generally worked up by injection molding, and in this field of injection molding, improvement of the productivity through reduction of the molding cycle or the so-called faster cycle is urgently called for.

For improvement of the mechanical strength of the polyoxymethylene resin, it is required to reduce the size of spherulites and homogenize the spherulite structure. For achieving a faster cycle, the method of accelerating the speed of crystallization and thus the speed of solidification in the mold is effective. For implementation of the finer and more homogenous crystalline structure and improvement of the speed of crystallization, there were proposed various methods of adding nucleating agents selected from inorganic compounds. For example, Japanese Patent Publication Nos. SHO59-129247 and SHO55-19942 disclose a method of using a branched or cross-linked polyoxymethylene resin as a nucleating agent, and Patent Publication No. SHO48-8254 describes addition of an inorganic compound represented by talc as a nucleating agent.

However, the resin compositions disclosed in the foregoing Japanese Patent Publication Nos. SHO59-129247, SHO55-19942 and SHO48-8254 do not have a sufficiently improved crystallization speed, so that a satisfactory improvement in cycle speed would not be expected and the improvement in mechanical strength through finer and more homogeneous crystalline structure of the obtainable mold is insufficient. Thus, they hardly satisfy the high mechanical strength required for application to electric and electronic equipment parts and automobile parts.

Summary of the Invention

The present invention provides a polyoxymethylene multi-copolymer particularly suitable for injection molding, allowing improved molding efficiency, in particular allowing a faster cycle performance and enabling molded products having improved mechanical properties to be obtained.

In particular the molded product may have the required crystallinity characteristics to provide the desired high mechanical strength and may also have excellent surface appearance.

To achieve this, there is provided, according to one aspect of the present invention, a polyoxymethylene multi-copolymer which is obtainable by copolymerizing:

- (a) trioxane;
 - (b) at least one cyclic ether or formal chosen from ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane and 1,3,6-trioxocane; and
 - (c) at least one compound chosen from the group comprised of glycidyl phenyl ether, styrene oxide and glycidyl naphthyl ether, and which is characterised in that the polyoxymethylene multi-copolymer is of a number average molecular weight of 10,000 to 100,000, that its melting temperature (T_m) and crystallization temperature (T_c) are governed by the relationship
- $$T_m - T_c < 15 (^{\circ}\text{C})$$

and that the spherulites are of a size of 10 μ m or less.

According to another aspect of the present invention, there is provided a polyoxymethylene resin composition comprising

(A) 100 parts by weight of a polyoxymethylene resin and

(B) 0.001 to 100 parts by weight of a polyoxymethylene multi-copolymer which is obtainable by copolymerizing:

(a) trioxane;

(b) at least one cyclic ethers or formal chosen from the group comprised of ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane and 1,3,6-trioxocane; and

(c) at least one compound chosen from the group comprised of glycidyl phenyl ether, styrene oxide and glycidyl naphthyl ether.

Furthermore, according to the present invention, there is also provided a molded product manufactured from the above polyoxymethylene multi-copolymer, or from a resin composition containing it.

Description of the Preferred Embodiment

First, the oxymethylene multi-copolymer will be described.

The method of manufacturing the oxymethylene multi-copolymer of the present invention is not particularly limited. For example, it can be produced by dissolving or suspending each of the components (a), (b) or (c) in an organic solvent such as cyclohexane, in an organic solvent such as cyclohexane, adding a Lewis acid catalyst for polymerization, then removing by decomposition the unstable terminals. Preferably, a method using no solvent at all but a self-cleaning type mixer for bulk polymerization, deactivating the catalyst with a hindered amine compound, then removing the unstable terminals by decomposition, is cited. As a Lewis acid catalyst, boron trifluoride, a hydrate of boron trifluoride, or a coordination compound of an organic compound having oxygen or sulfur atoms with boron trifluoride, is preferably used. The Lewis acid catalyst is added preferably in an amount of 0.001 to 0.1 part by weight or more preferably in an amount of 0.005 to 0.05 part by weight to 100 parts by weight of trioxane. The reaction temperature for bulk polymerization is preferably 60 to 120 $^{\circ}$ C or more preferably 60 to 90 $^{\circ}$ C. The hindered amine compound refers to any of the compounds having a hindered amine skeleton in the molecule such as bis(1,2,2,6,6-pentamethyl-4-piperidiny) sebacate, bis(2,2,6,6-tetramethyl-4-piperidiny) sebacate, succinyl dimethyl-1-(2-hydroxyethyl-2,2,6,6-tetramethylpiperidine) polycondensation product, and 1-[2-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-tetramethylpiperidine, and it is added preferably in an amount equivalent to 0.1 to 20 nitrogen atoms in the hindered amine compound per boron atom in the catalyst.

The amount of copolymerized component (b), namely at least one cyclic ether or formal compound chosen from ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane and 1,3,6-trioxocane, in the polyoxymethylene multi-copolymer of the present invention, is preferably 0.01 to 20 parts by weight or, more preferably, 0.1 to 7 parts by weight to 100 parts by weight of the component (a), namely trioxane. When it is less than 0.01 part by weight, the heat stability tends to decrease, and when it exceeds 20 parts by weight, it is difficult to obtain a polymer distinguished in mechanical strength, and so such an amount is not preferable.

The amount of copolymerized component (c), namely at least one compound chosen from glycidyl phenyl ether, styrene oxide and glycidyl naphthyl ether, in the polyoxymethylene multi-copolymer of the present invention, is preferably 0.001 to 10 parts by weight or, more preferably, 0.01 to 5 parts by weight to 100 parts by weight of the component (a), namely trioxane. When it is less than 0.001 part by weight, the effect of improvement for achieving a faster cycle is not appreciable, and when it exceeds 10 parts by weight, the impact strength decreases, and so such an amount is not preferable.

The polyoxymethylene multi-copolymer of the present invention is preferably of a number average molecular weight of 10,000 to 100,000 when it is independently used for molding. This number average molecular weight is obtainable by the MI value determined at 190 $^{\circ}$ C and under a load of 2190 g according to ASTM D1238 with a pellet dried in a 80 $^{\circ}$ C hot oven using the formula

$$M_n = 75000 - 16000 \times \ln(MI)$$

Mn: Number average molecular weight

MI: MI value

When the polyoxymethylene multi-copolymer is independently used for molding, if the number average molecular weight is greater than 100,000, the impact strength decreases, and so such is not suitable.

In order for the polyoxymethylene multi-copolymer of the present invention when present by itself to enable a sufficiently faster cycle moldability and improved mechanical properties to be achieved, it is required that the melting point (T_m) and the crystallization temperature (T_c) of the polyoxymethylene multi-copolymer be governed by the relationship

$$T_m - T_c < 15 (^{\circ}\text{C})$$

and that the spherulites be of a size of $10\mu\text{m}$ or less.

If $T_m - T_c$ is 15°C or greater, the speed of solidification in the mold is retarded, resulting in less effect of reducing the molding time, and if the size of spherulites exceeds $10\mu\text{m}$, there remains a considerable molding strain after injection molding, resulting in degradation of the mechanical properties.

For determination of the melting point (T_m) and crystallization temperature (T_c), the following method was employed, namely heating the sample in a nitrogen atmosphere at a temperature increasing from 80°C to 220°C at a rate of $10^{\circ}\text{C}/\text{minute}$, maintaining the sample at 220°C for 5 minutes, then lowering the temperature at a rate of $10^{\circ}\text{C}/\text{minute}$ to measure the crystallization temperature, and thereafter cooling to 110°C , then raising the temperature at a rate of $10^{\circ}\text{C}/\text{minute}$ to measure the melting point.

For determination of the size of the spherulites, the following method was employed, namely holding 10 mg of the polyoxymethylene multi-copolymer between cover glasses, heating on a hot stage and melting at 230°C for 1 minute, then lowering the temperature to 130°C at a rate of $10^{\circ}\text{C}/\text{minute}$ while observing through a polarizing microscope, then photomicrographing the produced crystals to obtain the spherulite size.

Next, a polyoxymethylene resin composition in accordance with the invention comprising (A) polyoxymethylene resin and (B) a polyoxymethylene multi-copolymer will be described.

First, the polyoxymethylene resin (A) will be described. The polyoxymethylene resin (A) used in the polyoxymethylene composition according to the present invention is an oxymethylene homopolymer or an oxymethylene copolymer comprising 85% by weight or more of an oxymethylene unit or units and 15% by weight or less of an oxymethylene unit or units having 2 to 8 adjacent carbon atoms.

The oxymethylene homopolymer may be produced by, for example, introducing substantially anhydrous formaldehyde to an organic solvent containing a basic polymerization catalyst such as an organic amine and carrying out the polymerization, then acetylating the terminals with acetic anhydride.

The oxymethylene copolymer may be produced by, for example, dissolving or suspending substantially anhydrous trioxane and a copolymeric component such as ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane or 1,3,6-trioxocane in an organic solvent such as cyclohexane and carrying out the polymerization with a Lewis catalyst such as boron trifluoride-diethyl etherate added, then decomposing and thus removing the unstable terminals. Preferably, there may be employed a method using no solvent at all but introducing trioxane, a copolymeric component and a pre-catalyst to a self-cleaning type mixer for bulk polymerization, then deactivating the catalyst with a hindered amine and removing the unstable terminals by decomposition.

The amount for copolymerization of the copolymeric component such as ethylene oxide, 1,3-dioxolane, 1,3,5-trioxepane or 1,3,6-trioxocane of the oxymethylene copolymer of the present invention is preferably 0.01 to 20 parts by weight, more preferably 0.1 to 7 parts by weight, for 100 parts by weight of trioxane. When it is less than 0.01 part by weight, the polymer yield tends to decrease at thermal stabilization, and when it is more than 20 parts by weight, it is difficult to obtain a polymer which is distinguished in mechanical strength.

The amount of addition of the polymerization catalyst is preferably 0.001 to 0.1 part by weight, more preferably 0.005 to 0.05 part by weight, for 100 parts by weight of trioxane.

The temperature for bulk polymerization is preferably within the range of 60 to 120°C , more preferably 60 to 90°C . After polymerization, it is preferable to deactivate the catalyst with a hindered amine, then remove the unstable terminals for decomposition.

The polyoxymethylene multi-copolymer (B), when it is used for a polyoxymethylene resin composition of the present invention containing the above polymer (A), need not have its number average molecular weight, T_m , T_c or spherulite size of the copolymer limited in any way, as it has when it is independently used for molding.

In such a case, the polyoxymethylene multi-copolymer (B) is added as a moldability improving agent or nucleating agent of the polyoxymethylene resin (A) so that it is not always required to have a number average molecular weight, T_m , T_c and spherulite size enough to form an excellent molded product in its own right.

However, it is preferable that the polyoxymethylene multi-copolymer (B) has, if possible, a number average molecular weight, T_m , T_c and spherulite size as described above, that is, an average molecular weight of 10,000 to 100,000 a T_m and T_c governed by the relationship $T_m - T_c < 15 (^{\circ}\text{C})$ and a spherulite

size of 10 μ m or less even when it is used as a moldability improving agent or nucleating agent.

A polyoxymethylene resin composition of the present invention may be provided by mixing the polyoxymethylene Resin (A) and polyoxymethylene multi-copolymer with each other in the form of pellets, powder or grains, then directly subjecting the mixture to melting, but a method of melt mixing by means of Banbury mixer, rolls or extruder can also be used. The mixing temperature is preferably 150 to 250°C, more preferably 180 to 200°C.

In the polyoxymethylene resin composition of the present invention, the content of the polyoxymethylene multi-copolymer is from 0.001 to 100 parts inclusive by weight for 100 parts by weight of the polyoxymethylene resin. If it is less than 0.001 part by weight, the multi-copolymer fails to provide a satisfactory effect as a nucleating agent, and so a sufficient mechanical strength as well as crystallization speed is not obtainable.

Polyoxymethylene resin compositions embodying the present invention as described above have a very distinguished mechanical strength, well balanced with the impact resistance. Such physical properties are provided because the polyoxymethylene multi-copolymer works as a nucleating agent to develop a fine and homogeneous crystalline structure.

Actually, in the crystalline structure of an injection molded product obtained from a conventional polyoxymethylene resin using no nucleating agent, the agent presents a structure of coarse spherulites of a size of 150 to 200 microns, but the polyoxymethylene resin composition of the present invention presents a fine and homogeneous spherulite structure of 60 microns or less. Furthermore, both Izod impact strength and tensile strength are improved by 10%. Also, the crystallization temperature is elevated by 2 to 8°C, and so the difference between the melting point and the crystallization temperature is reduced to 25°C or less when the oxymethylene homopolomer is used as the polyoxymethylene resin, or 18°C or less when the oxymethylene copolymer is used as the polyoxymethylene resin, so that it enables a reduction in the molding cycle in injection molding to be achieved.

Thus, according to the present invention, there is provided a polyoxymethylene resin composition having a fine and homogeneous spherulite structure and a high strength in uniform quality, and further it is one of the advantages that the classification or purification, which is required when an inorganic compound is used as a nucleating agent, is no longer required.

Also, in the polyoxymethylene multi-copolymer or polyoxymethylene resin composition of the present invention, there may be included, to such an extent that the object of the invention is not hindered, a known additive or additives such as an antioxidant such as a hindered phenol, phosphite, thioether or amine type; a weathering-proof agent such as a benzophenone, benzotriazole or hindered amine type; a formaldehyde scavenger such as melamine, dicyandiamide, a polyamide or a polyvinyl alcohol copolymer; a release agent such as a fluorine containing polymer, a silicone oil or a polyethylene wax; a colorant such as a dye or a pigment; an ultraviolet ray screening agent such as titanium oxide or carbon black; a reinforcing agent such as fiber glass, carbon fiber or potassium titanate fiber; a filler such as silica, clay, calcium carbonate, calcium sulfate or glass bead; a nucleating agent such as talc; a flame retardant; a plasticizer; an auxiliary adhesive agent; and/or a tackifier. Moreover, in order to further improve the mechanical strength of the polyoxymethylene copolymer of the present invention, any other thermoplastic polymer or thermoplastic elastomer may be incorporated.

Examples

The invention will now be described in more detail with reference to the following Examples. In the Examples, the "%" and "parts" are all based on weight. The molding cycle and mechanical properties were determined as described below.

o Molding cycle:

Using an injection molding machine having an injection capacity of 5 ounces (14.2g), square plates of 80 x 80 x 3 mm were molded with the cylinder temperature set to 190°C, mold temperature to 60°C, injection time to 5 seconds and the cooling time changed, and the cooling time at which the deformation due to four ejector pins was such that when three vertexes of the mold were placed on a plane, the deviation of the remaining one vertex from the plane would be 1 mm or less, was measured.

o Molding:

Using an injection molding machine having an injection capacity of 5 ounces (14.2g), ASTM No.1 dumbbell test specimens and Izod impact test specimens were molded, with the cylinder temperature set to 190 °C, mold temperature to 65 °C and molding cycle to 50 seconds, and in the test, the exterior of the ASTM No.1 dumbbell test specimens was visually inspected.

o Mechanical properties:

Using the ASTM No. 1 dumbbell test specimens obtained by the foregoing injection molding, the tensile strength was determined according to ASTM D638, and using the Izod impact test specimens, the impact strength was determined according to ASTM D256.

o MI value:

Using pellets dried in an oven at 80 °C for 3 hours, the MI value was determined according to ASTM D1238 at a temperature of 190 °C and under a load of 2160 g.

o Spherulite size:

The size was measured by placing 10 mg of the polyoxymethylene resin composition between cover glasses, heating on a hot stage to melt the same at 230 °C for 1 minute, then lowering the temperature to 130 °C at a rate of 10 °C/minute and observing the produced crystals through a polarizing microscope and photomicrographing the same.

o Melting point (Tm) and crystallization temperature (Tc):

Using a differential scanning calorimeter (DSC) and heating the composition from 80 °C to 220 °C at a rate of 10 °C/minute in nitrogen atmosphere, maintaining the temperature at 220 °C for 5 minutes, then lowering the temperature at a rate of 10 °C/minute, the crystallization temperature was measured. Further, cooling to 110 °C once, then raising the temperature at a rate of 10 °C/minute, the melting point was measured.

Examples 1 to 10 and Reference Examples 1 to 5.

Continuous polymerization was carried out with trioxane, a compound of the component (b), a compound of the component (c), boron trifluoride diethyl etherate in 100 ppm to trioxane (2.5% benzene solution) and methylal or modifier, fed to a 100mmØ, L/D=10 twin screw continuous mixer "S4 KRC Kneader" (product of Kurimoto Ltd.). The polymerization temperature was controlled to about 60 °C by feeding hot water to the jacket, and the speed of revolution was set at 60 rpm. The compound of the component (c) and methylal as a molecular weight regulator were dissolved in trioxane. Also, a preliminary mixing zone was provided so that the compound of the component (b) and the catalyst solution were preliminary admixed immediately before they were fed to the kneader. The polymer was obtained in the form of a white fine powder.

To 10 kg of the powder thus obtained, a solution of 27 g of bis(1,2,2,6,6-pentamethyl-4-piperidiny) sebacate dissolved in 200 ml of benzene was added to deactivate the catalyst, then 10 g of calcium stearate and 50 g of 1,6-hexanediol bis(3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate) ("Irganox" 259 of Chiba-Geigy) were added, and the mixture was stirred in a Henschel mixer for 10 minutes. Using a 35 mmØ, L/D=30 twin screw extrusion machine with a vent, the obtained mixture was melted and stabilized at a cylinder temperature of 230 °C and a vent vacuum of 5 Torr, then it was extruded into water, and by cutting, a polyoxymethylene copolymer was obtained in the form of pellets. Confirmation of the composition of the obtained polyoxymethylene copolymer was made by the 60 MHz ¹H NMR (in d₂-hexafluoroisopropanol solvent). For example, where glycidyl phenyl ether was used as the compound of the component (c), there

were detected a multiplet signal particular to phenyl group at δ 6.9-7.6 (ppm) in addition to a signal of methylene group at δ 4.3-5.2 (ppm), and so the copolymer was confirmed to be a glycidyl phenyl ether copolymer. Further, by the integration ratio, it was confirmed that the components were copolymerized according to the amounts of addition.

5 The copolymeric compositions and physical properties of the polyoxymethylene multi-copolymers thus obtained are shown in Table 1. From Table 1, it is apparent that the polyoxymethylene multi-copolymers according to the present invention have distinguished injection moldability and mechanical properties.

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Table 1

Copolymeric compositions of polyoxymethylene multi-copolymers (parts by weight)											
Trioxane	Component (b) compounds	Copolymeric amount	Component (c) compounds	Copolymer- ric amount	MI value (g/10 min)	T _g -T _c (°C)	Spherulite size (µm)	Holding cycle cooling time (sec)	Tensile strength (MPa)	Isod impact strength with V notch (J/m)	
Example 1	100	1,3-Dioxolane	3.0	Glycidyl phenyl ether	1.0	20.4	12.6	2	3.2	67.3	63.1
Example 2	100	1,3-Dioxolane	3.0	Styrene oxide	1.0	18.7	13.7	2	3.5	66.8	61.7
Example 3	100	1,3-Dioxolane	3.0	Glycidyl Naphthylether	1.0	23.4	14.1	2	3.7	63.4	60.5
Example 4	100	Ethylene oxide	3.0	Glycidyl phenyl ether	1.0	19.8	12.7	2	3.2	66.8	62.3
Example 5	100	1,3-Dioxepane	3.0	Glycidyl phenyl ether	1.0	22.7	13.2	2	3.5	65.4	61.6
Example 6	100	1,3,5-Trioxepane	3.0	Glycidyl phenyl ether	1.0	23.5	13.5	3	3.5	67.1	61.5
Example 7	100	1,3,6-Trioxocane	3.0	Glycidyl phenyl ether	1.0	22.1	13.3	3	3.5	66.0	61.7
Example 8	100	1,3-Dioxolane	1.0	Glycidyl phenyl ether	0.3	9.0	14.2	7	3.7	64.2	60.8
Example 9	100	1,3-Dioxolane	1.0	Glycidyl phenyl ether	3.0	52.1	10.7	2	3.0	68.1	58.0
Example 10	100	1,3-Dioxolane	1.3	Glycidyl phenyl ether	0.3	1.1	12.5	2	3.8	68.9	61.7
Reference 1	100	1,3-Dioxolane	3.0	-	-	9.2	22.3	170	5.5	56.3	52.4
Reference 2	100	1,3-Dioxolane	3.0	Glycidyl phenyl ether	0.0005	8.8	19.7	50	5.0	57.5	51.7
Reference 3	100	1,3-Dioxolane	3.0	Glycidyl phenyl ether	15	73.4	11.3	2	3.2	68.3	37.4
Reference 4	100	1,3-Dioxolane	0.005	Glycidyl phenyl ether	0.5	15.3	25.6	9	4.5	69.1	67.3
Reference 5	100	1,3-Dioxolane	25	Glycidyl phenyl ether	0.5	62.5	14.5	4	4.1	44.7	72.3

Examples 11 to 28 and Reference Examples 6 to 10

o Preparation of polyoxymethylene resin POM-1

To a twin screw extruder type polymerization machine (25 mm \varnothing L/D=10.2) were introduced trioxane (450 g/h), 1,3-dioxolane (14 g/h), 100 ppm of boron trifluoride diethyl etherate (2.5% benzene solution) for trioxane and 500 ppm of ethylal, and continuous polymerization was carried out. The polymerization temperature was controlled to about 75 °C by feeding hot water to the jacket, and the speed of revolution was set 100 rpm. Ethylal as a molecular weight regulator was dissolved in trioxane. Also, in order that 1,3-dioxolane and the catalyst solution would be preliminarily mixed with each other immediately before they were fed to the kneader, a preliminary mixing zone was provided. The polymer was obtained in the form of a white fine powder in an amount of 445 g/h.

To 1 kg of the fine powder thus obtained, a solution of 2.7 g of bis(1,2,2,6,6-pentamethyl-4-piperidiny) sebacate dissolved in 20 ml of benzene was added, and the mixture was stirred in a Henshel mixer for 10 minutes to deactivate the catalyst, then 5 g of Ciba-Geigy's "Irganox" 245 or triethylene glycol bis(3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate, 1 g of calcium stearate and 1 g of melamine were added. The mixture was heated with agitation at 210 °C for 10 minutes, and POM-1 was obtained.

o Preparation of polyoxymethylene resin POM-2

With polymerization carried out similarly to POM-1, the polymer discharged from the kneader was introduced into a 3% aqueous solution of ammonia and stirred. The polymer was filtered off and washed with water, then with acetone. Thereafter, it was introduced into a 10% aqueous solution of ammonia and then heated with agitation in an autoclave at 150 °C for 3 hours. After cooling to room temperature, the polymer was filtered out, washed with water then with acetone and dried, and POM-2 was obtained.

o Preparation of polyoxymethylene resin POM-3

n-Hexane was charged to a 30 cm diameter, 3 m depth polymerization vessel having stirring vanes and a formaldehyde supply nozzle provided on the bottom. Dissolving 0.5 part by weight of di-n-butyltin dimaleate in this, formaldehyde gas was introduced through the supply nozzle. The formaldehyde gas was provided by heat decomposition of paraformaldehyde at 140 to 180 °C and upon purification, and it was introduced at a rate of 1.5 kg/h. The temperature in the polymerization vessel was adjusted to 50 °C with cold or hot water fed to the jacket. In the polymerization vessel, there were gradually produced fine polymeric particles, but the polymer slurry was discharged, while the catalytic solution (n-hexane) was fed, so that the polymeric solid component was maintained at about 50% by weight. The withdrawn polymer was filtered out, washed thoroughly with water, then introduced in about 10 times its volume of acetic anhydride. Then, adding sodium acetate in an amount of 0.1% by weight of acetic anhydride, the mixture was heated at 139 °C for 5 hours, with agitation. When the reaction mixture cooled to room temperature, the polymer was filtered out, washed thoroughly with acetone and water, then dried, and POM-3 was obtained.

o Preparation of polyoxymethylene multi-copolymer (B)

Polymerization was carried out similarly to POM-1 except for the addition of another copolymeric unit, namely a compound of component (c), and a polyoxymethylene multi-copolymer (B) was obtained.

o Preparation of cross-linked POM

Except that 1,4-butanediol diglycidyl ether was additionally included, the polymerization was carried out similarly to POM-2, and a cross-linked POM was obtained.

All of the Reference Examples contained POM-1, but References 6 and 7 contained respectively no and too little multi-copolymer (B), references 8-10 contained, in place of multi-copolymer (B), a copolymer containing only components (a) and (b) (reference 8), a multi-copolymer in which component (c) was replaced by 1,4-butanediol diglycidyl ether, ie cross-linked POM (reference 9) and talc (reference 10).

Melting and kneading were carried out at 220 to 240 °C with a 45mm \varnothing , L/D=31.5 twin screw extruding machine with a vent used. The nature and proportions of amounts of component (c) of the multi-copolymer

(B) blended into the resin compositions of Examples 1-28, and the characteristics of the samples obtained, are shown in Table 2. Likewise, the nature and proportional amounts of the nucleating agent (where present) blended into Reference Examples 6-10, be it a polyoxymethylene copolymer, or cross-linked POM, or talc (added in place of the multi-copolymer) and the characteristics of the samples obtained, are shown in Table 3. Upon comparison of these Examples and Reference Examples with each other, it will be seen that the polyoxymethylene resin compositions having the polyoxymethylene multi-copolymer incorporated have a spherulite size greatly reduced and the crystallization temperature elevated by about 2 to 8°C and are distinguished in their mechanical strength and surface appearance.

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Table 2

Examples	Base POMs (100 parts by weight)	Compositions, MI values and additions of polyoxymethylene multi-copolymers				MI values (g/10 min)	Yield stress (MPa)	Izod impact strength (with V-notch) (J/m)	Spherulite size (μm)	Melting point T _m ($^{\circ}\text{C}$)	Crystallization temp. T _c ($^{\circ}\text{C}$)	T _m -T _c ($^{\circ}\text{C}$)	Surface appearance
		Copolymeric monomer	Copolymerized amount (wt%)	MI values (g/10 min)	Blending ratio (parts by weight)								
11	POM-1	GPE	0.001	9.0	1.0	9.0	61.5	58.4	19	164.1	147.9	16.2	Good
12			0.1	9.0	1.0	8.9	63.1	58.5	8	165.1	149.8	15.3	Good
13			0.3	9.3	0.3	9.0	62.9	59.8	5	163.1	147.9	15.2	Good
14			0.5	11.4	0.2	8.9	62.3	60.1	6	164.0	148.3	15.7	Good
15			1.0	10.3	0.001	8.9	61.7	57.9	17	165.9	149.2	15.7	Good
16			1.0	10.3	0.1	9.0	62.4	60.5	5	163.8	149.0	14.8	Good
17			1.0	10.3	0.3	9.0	63.8	61.2	3	164.2	149.3	14.9	Good
18			1.0	10.3	100	8.9	65.2	60.4	3	164.7	150.4	14.3	Good
19			10	50.3	0.01	9.0	63.6	60.2	4	163.4	149.3	14.1	Good
20		SO	0.3	8.8	0.3	8.9	62.0	59.1	7	164.2	149.0	15.2	Good
21	POM-2		1.0	22.1	0.1	9.0	63.8	60.6	6	163.8	148.5	15.3	Good
22		GNE	0.3	9.1	0.3	9.1	62.6	59.3	8	164.8	148.8	16.0	Good
23		GPE	0.3	9.3	0.3	8.9	62.8	60.2	5	164.7	149.5	15.2	Good
24			1.0	10.3	0.1	9.0	63.6	61.0	4	164.7	149.2	15.5	Good
25			1.0	10.3	0.3	9.0	63.8	60.5	3	164.8	149.5	15.3	Good
26	POM-3	GPE	0.3	9.3	0.3	15.2	73.1	69.8	10	175.4	152.3	23.1	Good
27			1.0	10.3	0.1	15.1	73.3	69.4	8	174.3	151.1	23.2	Good
28			1.0	10.3	0.3	15.0	74.0	70.1	7	174.5	152.4	22.1	Good

GPE: Glycidyl phenyl ether; SO: Styrene oxide; GNE: Glycidyl naphthyl ether

Table 3

References	Base POMs (100 parts by weight)	Compositions, <u>MI values</u> and <u>additions of polyoxymethylene multi-copolymers</u>				MI values (g/10 min)	Yield stress (MPa)	Izod Impact strength (with V-notch) (J/m)	Spherulite size (μm)	Melting point Tm (°C)	Crystallization temp. Tc (°C)	Tm-Tc (°C)	Surface appearance
		Copolymeric monomer	Copolymerized amount (wt%)	MI values (g/10 min)	Blending ratio (parts by weight)								
6	POM-1	--	--	-	--	9.2	56.3	52.4	170	165.2	142.9	22.9	Bad
7		GPE	0.0001	9.1	1.0	9.3	59.2	54.6	80	164.2	144.4	19.8	Slightly bad
8		BDE	1.0	10.3	0.0001	9.0	58.3	52.7	90	163.6	145.1	18.5	Slightly bad
9			1.0	0.9	0.1	8.0	58.0	53.5	70	165.0	146.0	19.0	Slightly bad
10		Talc		-	0.1	9.0	57.5	53.1	80	164.9	145.7	19.2	Bad
GPE: Glycidyl phenyl ether; BDE: 1,4-Butanediol diglycidyl ether (cross-linked POM)													

Claims

- 5 1. A polyoxymethylene multi-copolymer obtainable by copolymerization of
 - (a) trioxane
 - (b) at least one cyclic ether or formal chosen from ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane and 1,3,6-trioxocane, and
 - 10 (c) at least one compound chosen from glycidyl phenyl ether, styrene oxide and glycidyl naphthyl ether, which said multi-copolymer contains spherulites, characterised in that the number average molecular weight of said polyoxymethylene multi-copolymer is from 10,000 to 100,000, that the melting point (T_m) and crystallization temperature (T_c) thereof are governed by the relationship

$$T_m - T_c < 15 (^{\circ}\text{C})$$
 - 15 and that the spherulites are of a size of 10 μm or less.
2. A polyoxymethylene multi-copolymer according to claim 1, wherein the copolymeric amount of the cyclic ether or formal component (b) is 0.01 to 20 parts by weight for 100 parts by weight of the trioxane component (a).
3. A polyoxymethylene multi-copolymer according to claim 2, wherein the copolymeric amount of the cyclic ether or formal component (b) is 0.1 to 7 parts by weight for 100 parts by weight of the trioxane component (a).
4. A polyoxymethylene multi-copolymer according to any preceding claim, wherein the copolymeric amount of the component (c) is 0.001 to 10 parts by weight for 100 parts by weight of the trioxane component (a).
5. A polyoxymethylene multi-copolymer according to claim 4, wherein the copolymeric amount of the component (c) is 0.01 to 5 parts by weight for 100 parts by weight of a trioxane component (a).
- 25 6. A polyoxymethylene resin composition comprising:
 - (A) 100 parts by weight of a polyoxymethylene polymer; and
 - (B) 0.001 to 100 parts by weight of a polyoxymethylene multi-copolymer obtainable by copolymerizing
 - (a) trioxane
 - 30 (b) at least one cyclic ether or formal compound chosen from ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane and 1,3,6-trioxocane, and
 - (c) at least one compound chosen from glycidyl phenyl ether, styrene oxide and glycidyl naphthyl ether.
7. A polyoxymethylene resin composition according to claim 6, wherein the number average molecular weight of the polyoxymethylene multi-copolymer is from 10,000 to 100,000.
- 35 8. A polyoxymethylene resin composition according to claim 6 or 7, wherein the melting point (T_m) and crystallization temperature (T_c) of the polyoxymethylene multi-copolymer are in a relationship of $T_m - T_c < 15 (^{\circ}\text{C})$.
9. A polyoxymethylene resin composition according to claim 6, 7 or 8, wherein the polyoxymethylene multi-copolymer has spherulites of a size of 10 μm or less.
- 40 10. A polyoxymethyl resin composition according to any one of claims 6 to 9, wherein the polyoxymethylene polymer is an oxymethylene homopolymer.
11. A polyoxymethylene composition according to any one of claims 6 to 9, wherein the polyoxymethylene polymer is a copolymer comprising 85% by weight or more of an oxymethylene unit or units and 15% by weight or less of any oxyalkylene unit or units having 2 to 8 adjacent carbon atoms.
- 45 12. A molded product of a polyoxymethylene multi-copolymer having spherulites characterised in that said polyoxymethylene multi-copolymer is obtainable by copolymerizing
 - (a) trioxane,
 - (b) at least one cyclic ether or formal compound chosen from ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane and 1,3,6-trioxocane, and
 - 50 (c) at least one compound chosen from glycidyl phenyl ether, styrene oxide and glycidyl naphthyl ether, that the number average molecular weight of said polyoxymethylene multi-copolymer is from 10,000 to 100,000, that the melting point (T_m) and crystallization temperature (T_c) thereof governed by the relationship

$$T_m - T_c < 15 (^{\circ}\text{C})$$
 - 55 and that the size of the spherulites is 10 μm or less.
13. A moulded product according to claim 12, wherein the molding is an extrusion molding.
14. A molded product according to claim 12, wherein the molding is an injection molding.

15. A molded product of a polyoxymethylene resin composition comprising
- (A) 100 parts by weight of a polyoxymethylene polymer, and
 - (B) 0.001 to 100 parts by weight of a polyoxymethylene multi-copolymer obtainable by copolymerizing
 - (a) trioxane,
 - 5 (b) at least one cyclic ether or formal compound chosen from ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane and 1,3,6-trioxocane and
 - (c) at least one compound chosen from glycidyl phenyl ether, styrene oxide and glycidyl naphthyl ether.
16. A molded product according to claim 15, wherein the molding is an extrusion molding.
- 10 17. A molded product according to claim 15, wherein the molding is an injection molding.

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MEWBURN ELLIS 2 Cursitor Street
London EC4A 1BQ(GB)(54) **Polyoxymethylene multi-copolymer and its resin composition.**

(57) A polyoxymethylene multi-copolymer having spherulites and obtainable by copolymerizing

(a) trioxane,

(b) at least one cyclic ether or formal compound chosen from ethylene oxide, 1,3-dioxolane, 1,3-dioxepane, 1,3,5-trioxepane and 1,3,6-trioxocane, and

(c) at least one compound chosen from glycidyl phenyl ether, styrene oxide and glycidyl naphthyl ether, is characterised in that the number average molecular weight of said polyoxymethylene multi-copolymer is from 10,000 to 100,000, that the melting point (T_m) and crystallization temperature (T_c) thereof are governed by the relationship, $T_m - T_c < 15 (^{\circ}\text{C})$ and that the size of the spherulites is 10 μm or less,

and a resin composition comprising such a polyoxymethylene multi-copolymer and a polyoxymethylene resin, are distinguished in their crystallinity, mechanical strength and surface appearance and are particularly suited for faster cycle molding.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 275 604 (R.Y. KRAY ET AL) * column 2, line 4-29; claims 2,6,7,10; examples 3,4 * * column 3, line 55 - line 61 *	1-5, 12-14	C08G2/18 C08L59/04
X	DE-A-1 206 588 (DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT) * column 1, paragraph 1-3; claim *	1-5	
E	WORLD PATENTS INDEX LATEST Derwent Publications Ltd., London, GB; AN 90-302360 & JP-A-2 214 714 (NIHON TOKUSHU DOYAKU) 27 August 1990 * abstract *	1-5	
A	US-A-4 181 685 (R. KERN ET AL) * claim 1; examples *	1, 6, 10	
X	GB-A-971 916 (CELANESE CORPORATION OF AMERICA) * column 1, line 33 - column 2, line 63; claims; example 2 *	1-5, 12-17	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C08G C08L
A	US-A-4 427 807 (D. ZIMMERMANN AND SHAW-ZOU LU) * claims *	6-11	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25 MARCH 1992	Examiner KLIER E. K.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons @ : member of the same patent family, corresponding document	